



The College of New Jersey

Department of Chemistry

PO Box 7718
Ewing, NJ 08628-0718

Peer Review of Pacific Gas and Electric Company's Chromium Background Study Report, Hinckley Compressor Station

P) 609.771.2434
F) 609.637.5157
E) chem@tcnj.edu
W) www.tcnj.edu

Question 1. Quality of Spatial Sampling of Background Chromium

The sampling design is questionable. The purpose of this study was not to identify the primary source of Cr(VI) contamination, but to define the extent of the plume. To that end, more sampling should have occurred in the direction that the plume was believed to be directed toward rather than nearer to the known source. The sampling that did take place provides much more data than was required from sampling sites that were closest to the source, which biases the data summaries higher. This could seriously impact any conclusions based upon this data set regarding the extent and migration of the plume.

Question 2. Quality of Temporal Sampling of Background Chromium

The approach used in this study relative to the temporal trends appears to be reasonable. The use of an arithmetic mean to express the average concentrations of both total and hexavalent chromium is appropriate.

Question 3. Assumption of Statistical Normality

No comment, since this subject is outside my area of technical expertise

Question 4. Quality of Groundwater Modeling

As stated in the response to Question 1 above, the spatial sampling design that was used in this study is questionable.

The Big Picture – Additional Scientific Issues

The majority of my comments here are related to the efficacy and quality of the programmatic decisions regarding the choice of analytical methodologies and the quality of the data that was obtained.

The following questions were posed EMAX and Truesdale Laboratories, which were the two analytical laboratories that contributed data for this study. The questions that were posed were:

1. What calibration ranges were used for Methods 6010B, 6020A and 7199?
2. For Method 6020A, what was the value of the CRQL Check Standard (CRI) and the method control limits?
3. Were Reporting Limit (RL) check samples analyzed for Methods 7199 and 6010B?; if

so what are the control limits and what were the actual recoveries?

4. How were RLs established for Methods 6010B, 6020A and 7199? What is the relationship between the Method Detection Limit (MDL) & RL for each method?
5. What SRM was used for QC for 7199 as per Section 5.4? This data was apparently not reported.
6. Why were the spiking levels for both Cr(T) and Cr(VI) analyses MUCH higher than the expected sample concentrations for all analytical methods?

EMAX's responses to these questions were:

1. Responses are satisfactory
2. Response is satisfactory
- 3,4. Information on the RLs for Method 6020A were provided, but no information was supplied for Method 7199 or on how these limits were derived.
5. Response is satisfactory
6. This response was not satisfactory. The laboratory should have chosen the concentration level of matrix spikes for both Cr(T) and Cr(VI) to closer to the actual sample levels (usually a multiple of 3-5 the expected value is applied). The choice of much higher spiking levels means that the calculated recoveries have little value in assessing the quality of the actual sample concentrations and the impact to those results from possible matrix interferences.

Truesdale's responses to these questions were:

1. It is unclear from the response if the low level calibration ranges cited in the response for Methods 6010B and 6020A was used for the analyses in this study. If not, the data for this study for Cr(T) would be questionable.
2. Truesdale admitted in their response that they failed to perform this quality assurance as required by the method during the time that data for this study were obtained.
3. Truesdale admitted in their response that they failed to analyze a RL check sample during the time that data for this study were obtained.
4. Truesdale's response of varying criteria for a quantitative relationship between the MDL and RL is too vague to be acceptable.
5. The use of a mid-range check sample is NOT acceptable as a QC material as per the criteria for quality control specified in Method 7199. This would make the data for this study for Cr(VI) questionable.
6. This response was not satisfactory. The laboratory should have chosen the concentration level of matrix spikes for both Cr(T) and Cr(VI) to closer to the actual sample levels (usually a multiple of 3-5 the expected value is applied). The choice of much higher spiking levels means that the calculated recoveries have little value in assessing the quality of the actual sample concentrations and the impact to those results from possible matrix interferences

Other concerns with the analytical data that directly impact the conclusions of the study are:

1. No criteria were provide from with either laboratory as to the criteria for data assigned U or J flags
2. Based upon my experience with examining data for the analysis of Cr(VI) in water samples and soil extracts, this data set showed an unusually high percentage of samples failed the quality control criteria for the Continuing Calibration Verification (CCV). An explanation for this anomaly should be provided so as to show that the conclusions drawn from these data have not been compromised.
3. How were samples chosen for matrix spiking (was this procedure randomized so as to not bias the results?)
4. The workplan (Item #2 of Additional Materials) specifies the use of Method 6010 for the analysis of Cr(T); Method 6020A was used instead. This may impact the ability to quantify for Cr(T) at low concentration levels since the RL for Method 6020A is much lower than that for Method 6010.
5. Some data for Cr(VI) in this study was reported by the USEPA determinative method 218.6, other data was reported by Method 7196A and still other data was reported by Method 7199. These methods all have different sensitivities and different capabilities to report Cr(VI) without analytical interferences. Why were different methods used to measure Cr(VI)?
6. The rationale for using median vs. mean for data summaries was never provided.
7. The authors of the report chose to use a method from the United States Geological Survey (USGS) to attempt to define specific Cr species present in samples, any specie interconversion [either oxidation of Cr(III) to Cr(VI) or reduction of Cr(VI) to Cr(III)]. This method is not certified by any State or national laboratory accreditation authority. Information that was supplied suggests that this USGS method has only been applied to speciation of As. USEPA Method 6800, Elemental and Speciated Isotope Dilution Mass Spectrometry allows the identification individual Cr species, the extent of any specie interconversion, and can correct final results for up to 80% conversion. USEPA Method 6800 is certified by State and national laboratory accreditation authorities. Why was Method 6800 not used for this application?

Respectfully submitted,



Stuart Nagourney
Adjunct Professor of Chemistry
The College of New Jersey
Hillwood Lakes Campus
Ewing, New Jersey 08628
609-448-6440
nagourne@tcnj.edu

October 11, 2011

Attachments

From Truesdail Laboratory:

1) What calibration ranges were used for Methods 6010B, 6020A and 7199?

SW 6010B: Standard Calibration: 0.01 to 10 ppm
Low Level Calibration: 0.001 to 0.100 ppm

SW 6020A: Normally 0.2 to 500 ppb, or 0.2 to 100 or 200 ppb.

SW 7199: 0.2 to 50 ppb

2) For Method 6020A, what was the value of the CRI and the method control limits?

We were following the QAAP and there was no mention of this criteria. We started performing the CRI on September 12, 2011 and the criteria is $\pm 30\%$

3) Were RL check samples analyzed for Methods 7199 and 6010B?; if so what are the control limits and what were the actual recoveries?

SW 7199: Yes, control limits of $\pm 20\%$. The raw data was provided to CH2M Hill for these analysis but we were not asked to report them. A PQL sample was analyzed at 0.15 ug/L with control limits of $\pm 20\%$. The recoveries for the PQL in the data packages of interest were 108%, 110%, 103%, and 108%.

SW 6010B: We were not analyzing RL check sample. The Initial calibration starts with the PQL level and every 24 hours we run a calibration curve.

4) How were RLs established for Methods 6010B, 6020A and 7199? What is the relationship between the MDL & RL for each method?

The RL is 2 to 10 times the MDL depending on the noise level.

5) What SRM was used for QC for 7199 as per Section 5.4? This data was apparently not reported.

The mid-range calibration check standard (MRCCS) is a second QC source and is our QCS. It is the same thing but named differently and it is included in the package.

6) Why were the spiking levels for both Cr(T) and Cr(VI) analyses MUCH higher than the expected sample concentrations for all analytical methods?

For Cr(VI), we spike the sample using concentrations of 1, 5, 10, 25, etc., and use the spike concentration that is the next increment that is greater than or equal to the sample concentration. Ex. a sample concentration of 4.2 is spiked with 5 ppb.

For Cr(T): From the PG&E QAPP: "The spike levels will be less than or equal to the mid-point of the calibration range."

From SW 6020A: The spike levels should be "at approximately the mid-point of the linear dynamic range".

Re: Clarification of Analytical Issues

From: Anne Holden
To: Nagourney, Stuart
CC: Dernbach, Lisa; Kemper, Lauri
Date: Friday - September 16, 2011 3:33 PM
Subject: Re: Clarification of Analytical Issues

Hi Stuart

Hopefully now you have everything you need from Emax. I have let Truesdail lab know we are still expecting their responses, and to email them to Lisa Dernbach and Lauri Kemper, my supervisors. I will be out of the office until Oct 23! Thank you for your diligence in conducting the peer review.

If you have any other clarifications/questions, please email Lisa (ldernbach@waterboards.ca.gov) and Lauri (lkemper@waterboards.ca.gov). When they get the responses to your outstanding questions from Truesdail, they will forward them on to you and help transmit any followup questions you may have.

thanks again,
Anne

Anne Holden, P.G.
Engineering Geologist
Lahontan Water Board
<http://www.waterboards.ca.gov/lahontan/>
2501 Lake Tahoe Blvd.
South Lake Tahoe, CA 96150
530-542-5450 tel
530-542-5470 fax
aholden@waterboards.ca.gov

>>> Stuart Nagourney <nagourne@tcnj.edu> 9/14/2011 3:53 AM >>>

Ask the lab. to provide the data that shows that they are full compliance with Section 10.2.3.1 of USEPA Method 6020A.

----- Original Message -----

From: "Anne Holden" <AHolden@waterboards.ca.gov>
To: "Stuart Nagourney" <nagourne@tcnj.edu>
Sent: Tuesday, September 13, 2011 5:05:56 PM GMT -05:00 US/Canada Eastern
Subject: Re: Clarification of Analytical Issues

Please see attached, and the text below [the lab's response to your additional questions (apparently they were able to figure out what samples you were referring to)]:

I was able to locate one of the SDGs 06K142. Please see attached file.
Included in the attached file are:

1. LCS report for 06K142 Method 6020A - Lab sample IDs for LCS/LCSD are IMK021WL and

IMK021WC respectively.

2. Analytical sequence - proof that LCS are analyzed with the samples
3. Digestion log - proof that the LCS are prepared the same way as the samples
4. Certificate of Analysis - proof that the standards used for LCS are purchased as certified standards from CPI

Please note that all samples received at EMAX are processed the same way. Should you have any question or need additional info please let me know.

>>> Stuart Nagourney <nagourne@tcnj.edu> 9/13/2011 11:09 AM >>>

I have this info. @ home; I will get it to you later today.

----- Original Message -----

From: "Anne Holden" <AHolden@waterboards.ca.gov>

To: "Stuart Nagourney" <nagourne@tcnj.edu>

Sent: Tuesday, September 13, 2011 1:55:12 PM GMT -05:00 US/Canada Eastern

Subject: Re: Clarification of Analytical Issues

Hi Stuart

Here is the lab's response - can you provide the needed information to help them narrow down the research?

--I need some specific info to help me go through archived records. We archive records per SDG and all related document from the SDG including preplogs (will prove that LCS was digested with the field samples) and standard logs(to trace for the LCS vendor)can be located. If you can provide me the SDG or at least the sample ID then it will be easier to search.

>>> Stuart Nagourney <nagourne@tcnj.edu> 9/13/2011 7:48 AM >>>

Thanks.

For Question 5, please ask EMAX for 2 additional pieces of information: (1) what vendor was used for the lab. control sample and (2)for documentation that this lab. control sample sample was prepared in an identical manner to which the samples were subjected.

So you know, several of EMAX's responses are factually incorrect and that may compromise their data. I will include this information as part of my testimony.

I look forward to other laboratory's comments.

----- Original Message -----

From: "Anne Holden" <AHolden@waterboards.ca.gov>

To: "Stuart Nagourney" <nagourne@tcnj.edu>

Sent: Tuesday, September 13, 2011 10:09:42 AM GMT -05:00 US/Canada Eastern

Subject: Re: Clarification of Analytical Issues

Hello Stuart

Below are responses to your questions from EMAX labs: Truesdail is still working on their responses, I will forward those to you ASAP.

1) What calibration ranges were used for Methods 6010B, 6020A and 7199?

Response: Method 6020A (please note that EMAX did not use method 6010B for this project) for CAM metals and others, calibration ranges are: 10, 50 and 100 ug/L.
for Cations, Al and Fe, the calibration ranges are: 1000, 5000 and 10000 ug/L.
Method 7199; calibration ranges are: 0, 0.2, 2.0 and 5.0 ug/L.

2) For Method 6020A, what was the value of the CRI and the method control limits?

Response: CRI is not required for method 6020A hence it was not performed. All method QC requirements are applied, e.g., IECs, LDRs, ICSA, ICSAB, ICV, CCVs, LCS, MB, MS/MD, Dilution Test, Analytical Spike.

3) Were RL check samples analyzed for Methods 7199 and 6010B?; if so what are the control limits and what were the actual recoveries?

Response: RL check was not required by the project QAPP or method 7199 hence no RL check was performed for this project. All method QC requirements were performed, e.g., ICV, CCVs(90-110% recovery), MB, LCS, MS/MD.

4) How were RLs established for Methods 6010B, 6020A and 7199? What is the relationship between the MDL & RL for each method?

Response: RLs are derived from the lowest calibration point.

5) What SRM was used for QC for 7199 as per Section 5.4? This data was apparently not reported.

Response: EMAX reported LCS (lab control samples) purchased as certified standards from independent source ~ SRM

6) Why were the spiking levels for both Cr(T) and Cr(VI) analyses MUCH higher than the expected sample concentrations for all analytical methods?

Response: Spiking levels are not specified by the method and the project QAPP, hence lab SOP was applied. Furthermore, for practical reasons LCS/MS laboratory spike levels are set the same for all samples. Sample concentration levels are unknown, hence analyzing samples to determine levels for spiking are deemed greatly onerous (and can be translated to a more costly analysis) with no scientific added value. If the analytical run is under control the sample result will be the same whether or not the spike level were (or were not) within the expected concentration levels.

>>> Stuart Nagourney <nagourne@tcnj.edu> 8/29/2011 12:03 PM >>>

Just the questions w/introduction will suffice for now. If it turns out that I need more detail, we can always ask for that later,

Thanks!

----- Original Message -----

From: "Anne Holden" <AHolden@waterboards.ca.gov>

To: "Stuart Nagourney" <nagourne@tcnj.edu>

Sent: Monday, August 29, 2011 2:24:31 PM GMT -05:00 US/Canada Eastern

Subject: Re: Clarification of Analytical Issues

thanks Stuart - is it necessary (or helpful) for me to provide the labs with the chain of custody or lab analytical results for context, or just send the questions with an introductory paragraph?

>>> Stuart Nagourney <nagourne@tcnj.edu> 8/29/2011 10:57 AM >>>

Please ask the analytical laboratories to clarify the following issues:

- What calibration ranges were used for Methods 6010B, 6020A and 7199?
- For Method 6020A, what was the value of the CRI and the method control limits?
- Were RL check samples analyzed for Methods 7199 and 6010B?; if so what are the control limits and what were the actual recoveries?
- How were RLs established for Methods 6010B, 6020A and 7199? What is the relationship between the MDL & RL for each method?
- What SRM was used for QC for 7199 as per Section 5.4? This data was apparently not reported.
- Why were the spiking levels for both Cr(T) and Cr(VI) analyses MUCH higher than the expected sample concentrations for all analytical methods?

>>> Michael Ngo <michaeln@truesdail.com> 10/06/11 2:34 PM >>>

Hi Anne,

Sorry for the long delay. Attached is list of QC questions and their answers.

>>>

>>>

>>

On 9/16/2011 3:15 PM, Anne Holden wrote:

> Hello Mona and Michael--

> We'll be looking forward to receiving Truesdail lab's responses. I will be out of the office from Sept 16 through Oct 23. In my absence, please email the responses to Lisa Dernbach (ldernbach@waterboards.ca.gov) and Lauri Kemper (lkemper@waterboards.ca.gov), both of whom are cc'ed on this email.

>

> thank you

> --Anne

>

>

> _____
> Anne Holden, P.G.

> Engineering Geologist

> Lahontan Water Board

> <http://www.waterboards.ca.gov/lahontan/>

> 2501 Lake Tahoe Blvd.

> South Lake Tahoe, CA 96150

> 530-542-5450 tel

> 530-542-5470 fax

> aholden@waterboards.ca.gov

>

>

>

>>>> Mona Nassimi<mona@truesdail.com> 9/12/2011 10:09 AM>>>>

>>>>

> Dear Anne,

> This project is very high profile and we are waiting for our client to
> obtain their permission to respond to your questions. We apologize for
> any inconvenient and delay.

>

> Sincerely,

>

>

> Mona Nassimi

> Truesdail Laboratories, Inc

> Manager Analytical Service Division

> 714-730-6239

> 714-730-6462 Fax

> mona@truesdail.com<mailto:mona@truesdail.com>

> 14201 Franklin Ave

> Tustin, CA 92780

>

> >>

>>>>> Michael Ngo<michaeln@truesdail.com> 8/29/2011 3:43 PM>>>>>

>>>>>

>> Hi Anne,

>> We are working on getting those answers for you. I should be able to
>> send you answers for all of your questions by tomorrow.

>>

>>

>> Sincerely

>> Michael Ngo

>> Project Manager/Quality Assurance Manager

>> Truesdail Laboratories Inc.

>> Environmental Services

>> (714)730-6239

>> michaeln@truesdail.com

>>

>>

>> ----- Original Message -----

>> Subject: Re: QC questions

>> Date: Thu, 8 Sep 2011 17:38:18 -0400

>> From: Anne Holden<AHolden@waterboards.ca.gov>

>> To: Michael Ngo<michaeln@truesdail.com>

>>

>>

>>

>> Hi Michael

>> just following up on the status of your answers - any ETA?

>> thanks!

>>

>>

>> Anne Holden, P.G.

>> Engineering Geologist

>> Lahontan Water Board

>> <http://www.waterboards.ca.gov/lahontan/>

>> 2501 Lake Tahoe Blvd.

>> South Lake Tahoe, CA 96150

>> 530-542-5450 tel

>> 530-542-5470 fax

>> aholden@waterboards.ca.gov

>>

>>

>>

>>>>> Michael Ngo<michaeln@truesdail.com> 8/29/2011 3:43 PM>>>

>>>>>

>> Hi Anne,

>> We are working on getting those answers for you. I should be able to

>> send you answers for all of your questions by tomorrow.

>>

>>

>> On 8/29/2011 1:18 PM, Anne Holden wrote:

>>

>>> Hello Mr Ngo:

>>>

>>> I work for the Lahontan Regional Water Quality Control Board, a state of California agency. Our agency oversees the cleanup of chromium contamination in groundwater at the Pacific Gas and Electric Company Hinkley Compressor Station in Hinkley, CA. In 2006, PG&E conducted groundwater sampling to examine background chromium concentrations in the Hinkley area. We are reviewing the quality control

data for this sampling effort, which took place over four quarters of calendar year 2006. Your lab performed analytical chemistry services for the groundwater sampling, and we have the following questions regarding the analytical testing.

>>>

>>> 1) What calibration ranges were used for Methods 6010B, 6020A and 7199?

>>> 2) For Method 6020A, what was the value of the CRI and the method control limits?

>>> 3) Were RL check samples analyzed for Methods 7199 and 6010B?; if so what are the control limits and what were the actual recoveries?

>>> 4) How were RLs established for Methods 6010B, 6020A and 7199? What is the relationship between the MDL& RL for each method?

>>> 5) What SRM was used for QC for 7199 as per Section 5.4? This data was apparently not reported.

>>> 6) Why were the spiking levels for both Cr(T) and Cr(VI) analyses MUCH higher than the expected sample concentrations for all analytical methods?

>>>

>>> Please reply to each question above as they pertain to the services your lab performed. I would very much appreciate your reply as soon as possible. Please contact me with any questions or if you need more information to respond to this request.

>>>

>>> Regards,

>>>

>>>

>>>

>>> _____
>>> Anne Holden, P.G.

>>> Engineering Geologist

>>> Lahontan Water Board

>>> <http://www.waterboards.ca.gov/lahontan/>

>>> 2501 Lake Tahoe Blvd.

>>> South Lake Tahoe, CA 96150

>>> 530-542-5450 tel

>>> 530-542-5470 fax

>>> aholden@waterboards.ca.gov